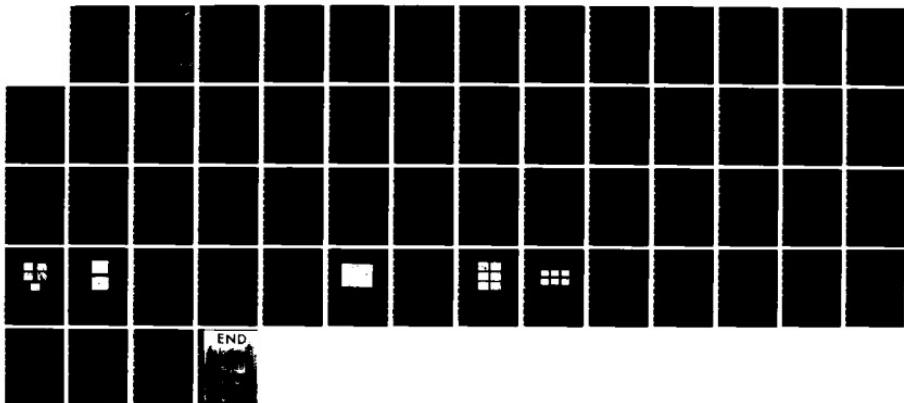


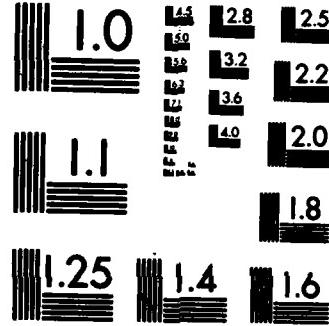
AD-A136 782 SILOXANE MODIFIERS FOR EPOXY RESINS(U) VIRGINIA
POLYTECHNIC INST AND STATE UNIV BLACKSBURG VA POLYMER
MATERIALS AND INTERFACES LAB E M YORKGITIS ET AL.
UNCLASSIFIED 01 DEC 83 TR-6 N00014-78-C-0629

1/1

F/G 11/9

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A136782

OFFICE OF NAVAL RESEARCH
Contract N00014-78-C-0629
Task No. NR 356-692

(12)

TECHNICAL REPORT NO. 6

Siloxane Modifiers for Epoxy Resins

by

*E. M. Yorkgitis, +C. Tran, #N. S. Eiss, Jr., #T. Y. Hu,
+I. Yilgor, *G. L. Wilkes, and +J. E. McGrath

*Department of Chemical Engineering,
+Department of Chemistry, and
#Department of Mechanical Engineering
Polymer Materials and Interfaces Laboratory
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-6496

December 1, 1983

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

DTIC
SELECTED
S D
JAN 16 1984

DTIC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
		AD-A136 782
4. TITLE (and Subtitle) Siloxane Modifiers for Epoxy Resins		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) E.M. Yorkgitis, C. Tran, N.S. Eiss, Jr., T. Y. Hu, I. Yilgor, G. L. Wilkes and J.E. McGrath		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0629 (Mod. # P00005)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Virginia Polytechnic Institute and State Univ. Blacksburg, VA 24061-6496		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-692
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy St., Arlington, VA 22217		12. REPORT DATE December 1, 1983
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution Unlimited, Approved for Public Release		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Epoxy, Siloxane, Adhesion, Toughening, Fracture		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Functionally terminated polydimethylsiloxane and its statistical copolymers with either methyltrifluoropropyl (TFP) or diphenyl siloxane have been used to chemically modify bisphenol A-based epoxy resins. Increasing the percentage of TFP or diphenyl units relative to the dimethyl siloxane content of the oligomers enhanced their compatibility with the epoxy resin. This in turn produced smaller rubber particle sizes and altered particle morphology. Improved fracture toughness relative to the cycloaliphatic diamine-cured control resin was achieved in resins modified with polysiloxane copolymers containing 40% or more		

Block No. 20 cont'd. (Abstract)

TFP content or 20% diphenyl siloxane. Comparisons in these and other aspects are made with similarly prepared ATBN- and CTBN-modified epoxies. Wear rate was quite dramatically reduced with some of the modifiers. Wear results are discussed in terms of the fatigue wear theory. ←

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A1	



ABSTRACT

Functionally terminated polydimethylsiloxane and its statistical copolymers with either methyltrifluoropropyl (TFP) or diphenyl siloxane have been used to chemically modify bisphenol A-based epoxy resins. Increasing the percentage of TFP or diphenyl units relative to the dimethyl siloxane content of the oligomers enhanced their compatibility with the epoxy resin. This in turn produced smaller rubber-particle sizes and altered particle morphology. Improved fracture toughness relative to the cycloaliphatic diamine-cured control resin was achieved in resins modified with polysiloxane copolymers containing 40% or more TFP content or 20% diphenyl siloxane. Comparisons in these and other aspects are made with similarly prepared ATBN- and CTBN-modified epoxies. Wear rate was quite dramatically reduced with some of the modifiers. Wear results are discussed in terms of the fatigue wear theory.

INTRODUCTION

Epoxy resins form a very important class of thermosetting polymers that often exhibit high tensile strength and modulus, excellent chemical and corrosion resistance, and good dimensional stability (1-3). However, these highly crosslinked systems are usually brittle and consequently have limited utility in applications requiring high impact and fracture strengths. Such applications include reinforced plastics, matrix resins for composites, and high performance coatings.

In recent years, the incorporation of elastomeric modifiers into the glassy epoxy matrix has served as a successful means of enhancing the fracture toughness and impact resistance of epoxy networks. Liquid butadiene acrylonitrile copolymers having both carboxyl (CTBN) and amine (ATBN) end groups have been widely used as epoxy modifiers (4-11). During the curing process, the elastomeric component separates within the reacting medium to form a second dispersed phase. Through various proposed mechanisms, these rubbery domains act to alleviate crack propagation under low loads. Investigators have found that the fracture energy of the base epoxy can often be significantly improved with the addition of as little as 5 percent of an elastomeric modifier (12,13). Furthermore, this improvement in fracture resistance can be achieved with little sacrifice in bulk properties.

In the present study, we are investigating liquid functional polysiloxanes as new modifiers for epoxy networks. Polydimethylsiloxanes are widely known to exhibit important characteristics such as low glass transition temperature (ca. -120°C), high flexibility, good weatherability, and good thermal and oxidative stability (14). In addition, due to their low surface energy and nonpolar structure, polysiloxanes tend to migrate to the air-polymer interface. This unique tendency for surface coverage

provides a very hydrophobic surface for the substrate. In light of these facts, one might also expect the presence of siloxane to strongly influence the friction and wear behavior of these modified resins.

Initial results on the synthesis and characterization of the siloxane-modified epoxy networks have already been presented (15) and will not be repeated here in detail. This paper extends those studies to polysiloxane copolymers containing not only dimethyl groups but also trifluoropropyl and diphenyl groups. As this is an ongoing research effort, this paper is meant to be an overview of the following topics: chemistry and synthesis, mechanical properties, fracture toughness, morphology, and friction and wear characterization. Each of these sub-topics will be discussed in more detail in future publications.

The glassy network system under investigation was obtained from the curing reaction of a bisphenol A diglycidyl ether-based epoxy resin (Epon resin 828) with a cycloaliphatic diamine, bis(4-aminocyclohexyl)methane (PACM-20). Figure 1 shows the chemical structure of the siloxane oligomers used in this study, which are synthesized in our laboratory. The present investigation is restricted to the use of the 2-aminoethylpiperazine (AEP) end group.

The solubility parameter of polydimethylsiloxane, about 7.5, has been estimated to be lower than that of bisphenol A epoxy resin, 9.4. The solubility parameter of the oligomer is considered to be a key factor governing its phase separation from the epoxy resin. Ideally, one would like to control the parameter in such a way that the siloxane oligomer will be miscible with the epoxy resin in the initial stages of cure but will phase separate during the later stages. It was expected that copolymerizing the more polar trifluoropropylmethyl siloxane unit with dimethylsiloxane would raise the solubility parameters closer to that of

the resin. A similar effect could also occur through use of the resonant structure of diphenylsiloxane.

The primary objective of rubber modification is the improvement of fracture properties with a minimal decrease in mechanical strength. As indicated above, this has been achieved in part with the use of the commercially available ATBN and CTBN (amino- and carboxy-terminated butadiene acrylonitrile) copolymers manufactured by the B. F. Goodrich Co. However, the relatively high glass transition temperatures of acrylonitrile butadiene copolymers limit their low temperature flexibility while their highly unsaturated structure makes them unsuitable for use at elevated temperatures (16,17). Siloxanes possess, among other attributes, lower glass transition temperatures than conventional elastomers. In addition, their thermal stability is very good.

Because a large proportion of the work on rubber-modified epoxies has dealt with the ATBN and CTBN materials, it seemed appropriate to study these modifiers along with the new siloxane oligomers. We therefore prepared networks that were essentially identical but for their modifier as will be elaborated on in the experimental section. For each modified resin, the quantities of flexural modulus, Young's modulus, and K_{IC} -- plane-strain fracture toughness -- were determined. The fracture surface morphology was examined as well.

The low surface energy of the chemically bound siloxane promotes a non-fugitive "slippery surface." This unique circumstance has led to our interest in the friction and wear characteristics of these siloxane-modified epoxies. Friction and wear are known to be functions of surface energy, toughness, and fatigue (18). Fatigue itself is thought to be a reflection of various factors including contact stress and elastic modulus. Tests designed to study the overall friction and wear phenomena

were performed using three variables: the normal load between two sliding surfaces, the percent rubber in the epoxy, and the percent of trifluoropropyl content in the siloxane modifier.

EXPERIMENTAL

Materials

The epoxy resin used was Epon resin 828, which was generously supplied by the Shell Chemical Co. The number average molecular weight of this diepoxide is about 380 g/mol. The curing agent was bis(4-aminocyclohexyl) methane (PACM-20) and was kindly donated by Du Pont. Siloxane oligomers of controlled molecular weights were synthesized in our laboratory with varying weight percents of dimethyl, trifluoropropyl (TFP), and diphenyl siloxane units. Dimethylsiloxane tetramer was obtained from Petrarch Systems, Inc. Trifluoropropyl methyl cyclic trimer was provided by the Silicone Division of the General Electric Company as was diphenylsiloxane tetramer. The actual percentage of a specific kind of siloxane unit in an oligomer can be calculated in relation to the entire oligomer, including its end groups. It may also be calculated in relation only to the siloxane units. Given the same oligomer, the number found by the first method will be smaller than that found by the second method. This effect is more pronounced at low molecular weights where the weight of the end groups is a more appreciable fraction of the total oligomeric weight.

The oligomers were prepared via equilibration reactions using base catalysts such as tetramethyl ammonium siloxanolate or potassium hydroxide. The TFP/dimethyl copolymers contained 0, 20, 40, and 70 weight percent TFP units, based on the total oligomeric weight. We have also prepared dimethyl/diphenyl siloxane copolymers containing 20% diphenyl oligomer. The oligomers were characterized by proton nmr and FTIR techniques. Number average molecular weights of the oligomers were determined by end group titration. All siloxane oligomers were viscous liquids at room temperature.

Siloxane-modified networks were prepared for mechanical and wear

testing via two steps. First a linear precursor was formed by reacting Epon 828 with the siloxane oligomer at 65°C for one hour under reduced pressure. Vacuum was applied to remove trapped air bubbles from the reaction mixture. Previous kinetic studies using DSC (19) have shown that the time of one hour to generate the precursor is more than adequate for all of the AEP end groups to completely react with the epoxy resin. The piperazine-terminated siloxane oligomers were shown to be much more reactive with the epoxy resin than was PACM-20. After allowing the siloxane-epoxy mixture to react for one hour, the curing agent was added and the mixture was rapidly stirred for five minutes under vacuum. This second step was conducted at 50°C.

The epoxy/siloxane/PACM-20 mixture was then poured into a hot RTV-silicone mold of the precise shapes to be used for either mechanical or wear tests. The mixture was cured at 160°C for 2.5 hours. In early studies, the glass transition temperature of the Epon 828/PACM-20 network was reported to be 150°C (20). Consequently, the curing time and temperature chosen were considered sufficient to provide enough mobility for the chain ends to react and form the crosslinked network. The concentration of the siloxane modifiers was varied to be 5, 10, or 15% by weight.

The B. F. Goodrich Co. kindly provided our laboratory with ATBN and CTBN rubbers of both low (10%) and high (17-18%) acrylonitrile (AN) content. Their reported molecular weights are about 3700. The ATBN oligomers are produced from CTBN oligomers of the same AN content and should therefore have just slightly higher molecular weights. Considerable disparity exists, however, between ATBN and CTBN titrated molecular weights due to the excess AEP remaining in the ATBN's after production. It is the titrated molecular weight which we have used to determine the appropriate

amount of curing agent for complete network formation. All networks, regardless of the oligomer used, were prepared identically. Hence all modified resins were subjected to the same criteria concerning the ratio of rubber to resin to curing agent and cured according to the same schedule.

The glass transition temperatures of samples were determined using a Perkin Elmer DSC at heating rates of either 10 or 20 deg/min, respectively.

Sample Designation

Each oligomer or modified resin can be described by two or three numbers, respectively. Figure 2 illustrates the employed shorthand. As an example, a sample containing 10% by weight of a 20% TFP siloxane rubber of molecular weight 2330 g/mol will be designated 10-2330-20F. The oligomer would be labelled 2330-20F. Note that the differences between specific types of siloxane copolymers are given by changes in the third number of the sample code while differences between the end groups of the butadiene oligomers are given in the first number of the code as demonstrated by the examples in the figure.

Mechanical Properties

Tensile moduli were measured from standard dog-bone samples (2.0 mm thickness, 4.7 mm width, and 22.0 mm gauge length) in a Model 1122 Instron at a crosshead speed (CHS) of 1.0 mm/min. Flexural modulus and fracture toughness were determined using a three-point bend geometry. The testing apparatus consisted of two aluminum/steel pieces attached to the Instron which was fitted with a tensile load cell. This device effectively performs an inverted three-point bend; the two side bars remain stationary above the sample as the central bar below the sample moves upward. Flexural samples measured ca. 52.0 x 1.7 x 13.1 mm. They were tested using a 2.54 cm span (distance between the two side bars) at a CHS of 1.0 mm/min.

Dimensions of fracture toughness samples were ca. 3.2 x 6.4 x 38.1 mm. A thin saw notch approximately 1 mm deep was cut into the center of the 3.2 mm side. Into this notch was placed a sharp one-sided razor blade which was tapped lightly to make a short "pre-crack." The CHS was 0.5 mm/min. All modulus and fracture toughness testing was done at ambient temperatures.

Scanning Electron Microscopy

Fracture surfaces of the various materials were examined in an ISI, Inc. Super III-A Scanning Electron Microscope (SEM). Untested samples were cold fractured by snapping after being submerged in liquid nitrogen for 10 minutes. Following fracture toughness testing, the pre-crack front regions of such samples were also studied by SEM.

Friction and Wear

Polysiloxane-modified networks were cast into plates 3 to 4 mm thick and 50 mm square. After casting, the plates were immersed in isopropanol for twenty minutes to remove any unreacted surface species or adsorbed substances and then stored in a desiccator overnight before testing.

The friction and wear testing was performed on a pin-on-disk machine (21) in which a stationary chromium steel sphere (pin), 3.2 mm diameter, was held in contact with the rotating epoxy plate (disk) as shown in Figure 3. Three normal loads were used: 2, 5, and 10 N, and the sliding speed was constant at 0.63 m/sec. The experiments were performed in laboratory air at 21-23°C. The frictional force encountered during testing deflected a cantilever beam holding the pin, and the deflection was detected by a proximity detector. When wear occurred, the sphere generated a groove in the epoxy disk. The wear was estimated by measuring the cross section profile of the groove with a surface profile meter. See Figure 3.

In most cases, wear did not occur at the beginning of the test. For a given sample, the number of cycles needed to initiate wear generally increased as the normal load decreased; in some cases no wear was detected even after 30 kilocycles (kc) of disk rotation. After wear began, the test was run for 14 kc, and the cross section profile measured every 2 kc. The wear was proportional to the number of cycles as shown in Figure 3. The slope of the wear versus cycles curve, as calculated by linear regression, is the wear rate. Ninety-five percent confidence limits of the wear rate were also calculated.

RESULTS AND DISCUSSION

The overall curing reaction generating the siloxane-modified epoxy network is depicted in Figure 4. In the first step, the piperazine-terminated siloxane oligomer was reacted with the epoxy resin to make a linear soluble precursor with epoxide end groups. Then the siloxane-epoxy adduct (plus the excess epoxy) was cured with PACM-20 which yielded the modified crosslinked network. Liquid siloxane oligomers of number average molecular weights from 1000 to 5000 g/mol have been utilized for epoxy modification, but only a few of these have been studied in depth. Table 1 shows the glass transition temperatures for the siloxane oligomers relevant to the present investigation. As expected, the glass transition temperatures of the oligomers increase with increasing TFP content. The glass transition temperatures of the siloxane-modified networks are shown in Table 2. Except for the samples modified exclusively with TFP units, the glass transition temperatures remained essentially unchanged with respect to the control sample. This finding indirectly implies that phase separation has occurred in these siloxane-modified epoxy networks, as was expected. The T_g depression seen for the networks modified with the 1500-70F and 3130-70F elastomers clearly indicates partial miscibility between the siloxane and epoxy phases.

The brittleness of epoxy networks is one of their most undesirable properties, and rubber modification seeks to remedy this particular drawback. Yet in relieving this weakness it is important to maintain as fully as possible their favorably high moduli and overall good mechanical strength. Figure 5 illustrates that siloxane and TFP siloxane modification only slightly influenced the flexural modulus of the unmodified epoxy. As expected, the flexural modulus decreases as rubber content increases. The rate at which it decreases depends at least partly on the TFP content of

the rubber. In order to understand this and later results, one must consider how changes in TFP content alter the compatibility between rubber and epoxy.

Pure PDMS possesses no polar groups across its silicon-oxygen chain. However, if one of the two methyl groups of a monomer unit is replaced with an electronegative TFP group, this latter group can couple with the remaining electron-releasing methyl group to create a dipole across the siloxane chain. The epoxy resin has a greater affinity for this new polar elastomer, and the attraction between the two grows as TFP content increases. The effect of this situation is two-fold. First, as TFP content is increased, additional siloxane will remain dissolved in the epoxy matrix after cure is complete. Secondly, again as TFP content goes up, the siloxane that does not actually dissolve in the matrix will precipitate out later in the curing reaction. Since the mobility of the network system diminishes continuously with cure time, at the point where incompatibility is reached, the elastomeric segments of each network chain can coalesce with only so many other such segments. The net result is a particle size that is inversely proportional to TFP content. This same argument holds true for explaining the effect of increasing acrylonitrile content on the particle size of ATBN and CTBN domains in cured epoxy resins.

Figure 6 shows representative cold snap fracture surfaces for the control and four TFP siloxane-modified epoxies at 15% rubber content. Particle size lowers as TFP content increases, from about 50 to less than 5 μm . Not only the size but the make-up of the particle has changed. At low TFP content, the rubber domains are not simply large but appear to be composites of both epoxy and elastomer. In studies of CTBN-modified epoxies, other workers have found evidence for this type of domain by

viewing stained thin sections using transmission electron microscopy (22). At 70% TFP content, the siloxane oligomers form small particles which appear uniform in composition.

While molecular weight effects have not been emphasized in this research, we do note here the primary effect of increasing molecular weight. Figure 7 illustrates that doubling the molecular weight of a 70% TFP siloxane modifier introduces a few large particles while maintaining the small particles found alone at the 1500 molecular weight. Compare the upper and lower micrographs in Figure 7.

A second factor at work here is the glass transition temperature of the oligomer. As shown in Table 1, the Tg of the oligomers increases dramatically with TFP content, from -126 for the 2190-0 oligomer to -45°C for 1500-70F. A rubber inclusion having a higher Tg also possesses a higher modulus and thus has a less detrimental effect on the modulus of the base resin. The role of Tg, aside from compatibility effects, is great enough to sponsor our interest in copolymers of dimethylsiloxane and the relatively stiff diphenylsiloxane. Preliminary results for a 2250-20D oligomer will be given later in this paper.

Figure 8 gives flexural modulus data for the CTBN- and ATBN- modified epoxies. Again modulus drops with increasing rubber content. Within error, the effect of increasing AN content appears to parallel that of increasing TFP content in the siloxanes. In comparing the results of Figure 8 with those in Figure 5, which are drawn on identical scales, one may note that the values for the TFP siloxane-modified resins are generally higher than those for the butadiene-modified resins. This effect is rather subtle, but it is, in fact, reinforced by Young's modulus data, the latter of which is given in Table 3.

These differences may be at least partially explained by DSC data such

as that in Figure 9. One observes that the glass transition regions of the ATBN- and CTCN-modified epoxies are considerably broader and have a lower mid-point than those of the control and two siloxane-modified resins. This suggests that the butadiene oligomers are partially miscible with the epoxy and can soften it, thereby generally lowering its modulus somewhat more than do the siloxane modifiers.

Fracture toughness was monitored through K_{Ic} , plane-strain fracture toughness. K_{Ic} values for at least five samples of each material were calculated according to Knott (23):

$$K_{Ic} = \frac{6 P}{B W^{1/2}} f\left(\frac{a}{W}\right) \quad (1)$$

where P is the critical load, B is the sample's width, W is its thickness, and a is the length of the pre-crack. In this study, P is taken to be the load at break. Letting $R = a/w$, the geometry factor $Y = f(a/w)$ can be given as

$$Y = 1.93^{1/2} - 3.07 R^{3/2} + 14.53 R^{5/2} - 25.11 R^{7/2} + 25.80 R^{9/2} \quad (2)$$

The criteria of ASTM E399 were followed as closely as possible. The only criterion which could not always be satisfied was that for a straight pre-crack front, give or take 5%.

When graphically presenting K_{Ic} results, the error bars given for the control are typical of all those data points which do not have their own error bars. For samples containing 15% rubber, error was sometimes greater than 10%, and individual error bars are provided and labelled with the corresponding symbol. Such a large deviation results from the violation of the homogeneity criterion of linear elastic fracture mechanics at 15% of certain oligomers.

Given in Figure 10 are K_{IC} results on the TFP siloxanes. It is seen that modification with pure PDMS lowers K_{IC} almost linearly with rubber content. After an initial increase at 5% rubber, modification with the 2330-20F oligomer lowers K_{IC} in a linear fashion. As TFP content is raised to 40 and 70%, however, K_{IC} improves considerably, reaching a high value in the 10-2070-40F material. Because the K_{IC} value is quantitatively derived from processes occurring in the pre-crack front, these fronts were examined using SEM. Figure 11 shows two of the outstanding morphological features observed.

The first of these features is illustrated by Figure 11a, an example of a pre-crack front of the 10-2330-20F material, which showed a K_{IC} value below that of the control. One notes particularly the large composite particles of both epoxy and elastomer. These particles, rather than absorbing the energy of fracture, tear instead at some small angle to the direction of crack propagation. Tearing is not, in this case, entirely unexpected, as it is well known that many siloxane elastomers have relatively poor tear resistance at room temperature (14,24).

The second morphological feature which we wish to point out is pictured in Figure 11b. The micrograph exemplifies the K_{IC} fracture surface of the 15-1500-70F material, which gave a K_{IC} value above that of the control. The holes which cover the surface shown are examples of what has commonly been called the dilatation effect (25). Under the application of a triaxial stress, the matrix surrounding the rubber is believed to soften and dilate. The rubber inclusion also dilates, but once the stress has passed, the rubber -- which is still above its T_g -- collapses close to its original points of attachment within the matrix, forming the characteristic holes or cavities.

Superimposing K_{IC} data for the 2070-40F oligomer on the data from the ATBN and CTBN oligomers in Figure 12, we find that this particular

siloxane oligomer is quite competitive with the butadiene oligomers at both 5 and 10% rubber content. SEM micrographs reveal that although some composite particles are found in this material, there are also many small and presumably homogeneous rubber domains. (Data given in Figure 12 for the 2250-20D oligomer will be discussed later.)

Addressing strictly the butadiene oligomers, one sees from Figure 12 that at high AN content, the CTBN-modified resins have higher K_{IC} values than the ATBN-modified resins. However, at low AN content, the K_{IC} values of the ATBN-modified systems are higher than those of the CTBN-modified resins. As would be expected and has been shown by others, increasing AN content lowers particle size. And as weight percent of the rubber is increased, the number of domains increases as well.

Close examination of the ATBN and CTBN domains revealed a somewhat unexpected difference in particle morphologies. This result may well explain the switch-over in K_{IC} values just discussed. As an example, Figure 13 gives low magnification micrographs of resins modified with 10% of each of the four butadiene rubbers. While three of the samples show exclusively small particle morphology, the 10C-3690-10AN sample contains large composite rubber particles which coexist with small particles. The lower micrographs in Figure 13 clarify the nature of these small particles. For the CTBN's of either AN content, these small particles have a homogeneous texture. However, while ATBN incorporation never gives rise to large composite particles, its small particles appear to be small composite partic.es. It is interesting to note that the diameters of these small particles are roughly equivalent regardless of their morphological texture. It is not clear at this time exactly from what this difference follows, i.e., whether from the excess AEP in the ATBN or the amino vs. carboxy end groups or a combination of the two. We plan to extract AEP from the ATBN

elastomer, prepare a second series of ATBN-modified networks, and study the resultant morphology.

Figure 12 also presents K_{Ic} results on a siloxane containing 20% diphenylsiloxane units. With a modifier of only 20% diphenyl content, the K_{Ic} values are amongst the best seen for any of the siloxane modifiers thus far. The micrographs in Figure 14 exhibit the small particle morphology of these materials. Such a morphology was anticipated. Certainly the more hindered, bulky, and slightly polar diphenylsiloxanes have higher Tg's than the mobile dimethyl or even the methyltrifluoropropyl siloxanes. Thus during cure, phase separation is somewhat more difficult. No tearing of the 2250-20D domains was observed which may also be due to their high Tg relative to the softer and lower Tg PDMS modifiers. In addition, estimates of the solubility parameter of diphenylsiloxane place it very close to that of the epoxy itself. These two characteristics appear to encourage good modifying properties. Future work in this area will especially focus on these copolymeric modifiers.

Let us now turn our attention to investigations of the friction and wear behavior of these materials. In Figure 15, the wear rates are plotted versus the percent rubber for the three normal loads of 2, 5, and 10 N and TFP percentages of 0, 20, 30, and 70. To determine the main effect of the percent rubber on the wear rate, the wear rates at different loads and percent TFP were averaged at each percent rubber. (See Figure 16.) In an analogous manner, the main effect of percent TFP was calculated and is plotted in Figure 17. The interaction between percent rubber and percent TFP was obtained by averaging the wear rates at the different loads for each combination of percent rubber and percent TFP. (See Figure 18.)

The coefficient of friction for the unmodified epoxy did not vary significantly with normal load. For the polysiloxane-modified epoxies,

increasing the load from 2 to 10 N lowered the coefficient of friction between 22 and 46 percent. Although the coefficient of friction did not change for increases in percent rubber and percent TFP in the rubber at the 2 and 5 N loads, a significant change was found at the 10 N load. (See Figure 19.)

The interpretation of the friction and wear data first required the identification of the predominant wear mechanism. The three most prevalent mechanisms are adhesive transfer, abrasive cutting, and fatigue. Of these three, only fatigue is consistent with the observation that an initiation time is required before wear occurs. Fatigue wear has been shown to be proportional to the stress in the polymer raised to a power t where t varies from 2 to 8 depending on the polymer (18). The stress is usually estimated by using an elastic model of contact stress (Hertzian contact) which predicts that the stress is proportional to the one-third power of the normal load P and the two-thirds power of the elastic modulus E . The relationships between fatigue wear rate, stress, modulus, and load are given in Equation 3.

$$\text{WEAR RATE} = (\text{STRESS})^t = P^{t/3} E^{2t/3} \quad (3)$$

For a brittle polymer such as polymethylmethacrylate, t equals 8.

The data in Figure 15 clearly show that the wear rate increased as the normal load increased. The wear rates and elastic moduli for the materials used in the wear studies are given in Table 4. One will note from the table that the wear rate decreased with the modulus. Thus the variations in wear rate with the normal load and with the elastic modulus agree with the trends predicted by the fatigue wear theory.

An additional factor which could reduce the wear rate as the percent

rubber increases is the reduction in surface energy caused by the rubber components. When sliding starts on the as-cast sample, the surface is already enriched with the rubber components which migrated there during the curing process. After wear starts and the original surface is removed, the slider encounters the rubber domains and smears them over the epoxy surface, thus renewing the rubber-rich surface that existed on the as-cast surface. Such smearing is suggested by SEM micrographs of the wear tracks. The lower surface energy of the rubber compared to that of the epoxy would then decrease the adhesive forces, thereby lowering the stress on the surface. This lower stress results in a decrease in wear rate according to the fatigue wear theory.

A thorough study of the wear behavior of ATBN- and CTBN-modified epoxies is forthcoming. Preliminary work with 15C-3880-17AN and 15A-1750-18AN at 5 N loads showed that wear tracks formed before 2000 cycles had been completed. Thus no initiation time was seen in contrast to most of the siloxane-modified epoxies which required up to 30,000 cycles for the formation of a wear groove.

The reduction in friction coefficient with increasing percent rubber (Figure 19) is also consistent with a reduction in surface energy and tangential stress at the surface. One component of friction is the product of the shear strength of the interface and the area of contact at the interface. Thus, if the shear strength is reduced due to the presence of rubber on the surface, the friction should also be reduced.

Interactions between the percent rubber and percent TFP pertaining to the wear and friction are illustrated in Figures 18 and 19, respectively. No significant difference in wear or friction was observed for a resin containing 5% rubber of either 0 or 20% TFP content. However, at 10 and 15% rubber content, the 20% TFP oligomer reduces both friction and wear

compared to the 0% TFP oligomer. The wear results are consistent with the elastic modulus changes shown in Table 4. The friction data show that a minimum rubber content between 5 and 10% is necessary before the addition of TFP units significantly lowers the coefficient of friction.

For TFP percentages greater than 20, the wear rate increases and is a maximum at 70% TFP content. However, the data at 70% TFP must be analyzed with caution because the molecular weight of this modifier is much lower than that of the other oligomers. From these limited results, one sees that the elastic modulus at 70% TFP is greater than that at 20% TFP; thus the wear results are still consistent with the changes in elastic modulus. The 70% TFP sample also has a significantly different morphology than the other friction and wear samples; the domains are smaller and more uniformly dispersed. (See Figures 6 and 7).

CONCLUSIONS

Dimethyl, co-dimethyl/TFP, and co-dimethyl/diphenyl siloxane oligomers with aminoethylpiperazine end groups were prepared and used as modifiers for epoxy networks based on Epon 828 resin and PACM-20 hardener. Glass transition temperatures of the TFP/dimethyl oligomers increased with TFP content as expected. DSC studies of the TFP siloxane-modified epoxies indicated that phase separation had indeed occurred, however, high levels of TFP at relatively low molecular weights did depress T_g somewhat, implying partial miscibility.

Morphological changes were investigated by viewing fracture surfaces of the networks using SEM. We have found that increasing TFP content in the siloxane modifiers lowers the size of the rubber domains in the modified resins, indicating that, as intended, increasing TFP content enhances the siloxane's compatibility with the resin. The effects of increasing TFP content are analogous to raising acrylonitrile (AN) content in the ATBN- and CTBN-modified resins.

For all modifiers, flexural and Young's moduli have been found to decrease with increasing rubber content. The decrease is less severe as either TFP or AN content in the modifier is increased. It was observed that the flexural and Young's moduli of the ATBN- and CTBN-modified epoxies were generally lower than those of the TFP siloxane-modified resins. DSC traces suggested that this difference resulted from the partial miscibility of the ATBN and CTBN oligomers with the cured epoxy resin system.

Plane-strain fracture toughness (K_{IC}) values of the modified resins were most strongly influenced by the weight percent of the modifier and the apparent compatibility of the modifier with the resin. As TFP content was increased in the TFP/dimethyl oligomers, K_{IC} values climbed from below the K_{IC} of the unmodified control resin to values above that of the

control. The greatest improvement in K_{IC} was realized using a 40% TFP siloxane while 70% TFP siloxanes produced reasonable improvement. K_{IC} values of epoxy modified with a 20% diphenyl siloxane were -- at all weight percents of rubber -- superior to the control's value.

Low K_{IC} values in the siloxane-modified resins were primarily associated with large composite resin-rubber particles which tore under experimental conditions. Good K_{IC} values were predominantly traced to small homogeneous particles which dilated under fracture stresses.

Incorporation of ATBN and CTBN oligomers into the glassy networks raised K_{IC} relative to the control. The CTBN-modified resins exhibited higher K_{IC} values than the ATBN-modified systems at 17-18% AN content, but, at 10% AN content, the opposite was true. This reversal is thought to be related to a corresponding change in morphology.

SEM study showed that the ATBN-modified resins possess small resin-rubber composite particles at both 10 and 18% AN content. In contrast, the CTBN-modified epoxies exhibited homogeneous rubber domains at 17% AN content, but, at the lower AN level, developed large resin-rubber particles which co-existed with the small homogeneous particles.

The wear of the siloxane-modified epoxies was dominated by a fatigue mechanism in which an initiation period of sliding occurred before wear started. The wear rate correlated positively with changes in the normal load and elastic modulus as predicted by the fatigue wear theory. For the normal loads tested, the wear rate was lowest at 15% rubber content which contained 20% TFP.

The friction coefficient was reduced by increasing the percent rubber, and, at 10 and 15% rubber, was reduced further by increasing the percent TFP from 0 to 20%. The friction drop was assumed to be caused by the lowering of surface energy as rubber was spread over the epoxy during

sliding. This particular conclusion is consistent with our earlier publication in this area (15).

ACKNOWLEDGEMENT

The authors would like to acknowledge the generous financial support provided by the Office of Naval Research under Contract # N00014-78-C-0629-P00005.

LITERATURE CITED

1. Potter, W. G. "Epoxide Resins"; Springer-Verlag: New York, 1970.
2. "Epoxy Resin Chemistry and Technology"; May, C. A.; Tanaka, Y., Eds.; Marcel Dekker: New York, 1973.
3. "Epoxy Resin Chemistry"; Bauer, R. S., Ed.; ADVANCES IN CHEMISTRY No. 114; American Chemical Society: Washington, D.C., 1979.
4. Rowe, E. H.; Siebert, A. R.; Drake, R. S. Mod. Plast. 1970, 47, 110.
5. Riew, C. K.; Rowe, E. H.; Siebert, A. R. in "Toughness and Brittleness of Plastics"; Deanin, R. D.; Crugnola, A. M., Eds.; ADVANCES IN CHEMISTRY No. 154, American Chemical Society: Washington, D.C., 1976; p. 326.
6. Bucknall, C. B.; Yoshii, T. British Polymer J. 1978, 10, 53.
7. Riew, C. K. Rubber Chem. Tech. 1981, 54, 374.
8. Daly, J.; Pethrick, R.A.; Fuller, P.; Cunliffe, A. V.; Datla, P. K. Polymer 1981, 22, 32.
9. Sayre, J. A.; Assink, R. A.; Lagasse, R. R. Polymer 1981, 22, 87.
10. Bascom, W. D.; Cottingham, R. L. J. Adhesion 1976, 7, 333.
11. Sultan, J. M., McGarry, F. Polym. Eng. Sci. 1973, 13, 29.
12. Bascom, W. D.; Ting, R. Y.; Moulton, R. J.; Riew, C. K.; Siebert, A. R. J. Mater. Sci. 1981, 16, 2657.
13. Kunz, S. C.; Sayre, J. A.; Assink, R. A. Polymer 1982, 23, 1897.
14. Warrick, E. L.; Pierce, O. L.; Polmanteer, K. E.; Saam, J. C. Rubber Chem. Tech. 1979, 52, 437.
15. Riffle, J. S.; Yilgor, I.; Bantia, A. K.; Tran, C.; Wilkes, G. L.; McGrath, J. E. in "Epoxy Resin Chemistry II"; Bauer, R. S., Ed.; ACS SYMPOSIUM SERIES No. 221, American Chemical Society: Washington, D.C., 1982, p. 21.
16. Okamoto, Y. Polym. Eng. Sci. 1983, 23, 222.
17. Creed, K. E., Jr.; Neutron Devices Dept., General Electric Co., St. Petersburg, FL; INIS Atomindex 1980, 11(8), Abst. No. 517048, 1982.
18. Lancaster, J. K. Plastics and Polymers 1973, 41(12), 297-306.
19. Riffle, J. S.; Yilgor, I.; Bantia, A. K.; Wilkes, G. L.; McGrath, J. E. Am. Chem. Soc., Div. Org. Coat. Appl. Polym. Sci. 1982, 46, 397.
20. Yilgor, I.; Yilgor, E.; Bantia, A. K.; Wilkes, G. L.; McGrath, J. E. Polym. Bull. 1981, 4, 323.
21. Eiss, N. S., Jr.; Milloy, S. C. in "Wear of Materials, 1983"; Ludema, K. C., Ed.; ASME: New York, 1983.
22. Manzione, L. T.; Gillham, J. K.; McPherson, C. A. J. Appl. Polym. Sci. 1981, 26, 889, 907.
23. Knott, J. F. "Fundamentals of Fracture Mechanics"; John Wiley & Sons: New York, 1973; Chap. 5.

24. Gent, A. N.; Tobias, R. H. in "Elastomers and Rubber Elasticity"; Mark, J. E.; Lal, J., Eds.; ACS SYMPOSIUM SERIES, No. 193, American Chemical Society, Washington, D. C., 1982, p. 367.
25. Bucknall, C. B. "Toughened Plastics"; Applied Science Publishers, Ltd.: London, 1977.

LIST OF FIGURES

- Figure 1. Chemical structures of siloxane oligomers.
- Figure 2. Sample nomenclature for oligomers and modified resins.
- Figure 3. Wear (cross section area) as a function of the number of cycles of disk rotation.
- Figure 4. Synthesis of a siloxane-modified epoxy resin.
- Figure 5. Changes in flexural modulus with rubber content and TFP percentage in rubber. Error bars on data point for control are typical for all data points. Crosshead speed is 1.0 mm/min.
- Figure 6. SEM cold snap fracture surfaces for unmodified resin control and four siloxane-modified resins. Original magnification is 300X.
- Figure 7. SEM cold snap fracture surfaces for 15-1500-70F and 15-3130-70F. Original magnification is 300X.
- Figure 8. Changes in flexural modulus with rubber content and acrylonitrile (AN) percentage in ATBN and CTBN rubbers. Error bars on data point for control are typical for all data points. Crosshead speed is 1.0 mm/min.
- Figure 9. Normalized DSC traces of control and resin modified with 15% of one of six different oligomers. Six of the curves have been shifted vertically.
- Figure 10. Changes in K_{Ic} with rubber content and TFP percentage in rubber. See text for explanation of error bar usage. Crosshead speed is 0.5 mm/min.
- Figure 11. SEM micrographs of pre-crack fronts of fracture toughness specimens: a) 10-2330-20F and b) 15-1500-70F. Ellipses highlight torn rubber domain. Arrows indicate direction of crack propagation. Original magnification is 300X.
- Figure 12. Changes in K_{Ic} with rubber content for resin modified with ATBN, CTBN, 2070-40F, and 2250-20D. See text for explanation of error bar usage. Crosshead speed is 0.5 mm/min.
- Figure 13. Upper four photomicrographs are low magnification views of K_{Ic} fracture surfaces of resin modified with 10% of each butadiene oligomer. Lower two micrographs magnify the small particles of the two high AN oligomers, elucidating the differences in small particle make-up between the ATBN- and CTBN-modified resins. Original magnifications of upper four are 300X, of lower two, 10,000X.

- Figure 14. SEM micrographs of pre-crack fronts of resin modified with 2250-20D oligomer. Rubber contents are increasing from 5 to 10 to 15 weight percent moving from left to right. Original magnification of upper row is 300X, of lower row, 3000X.
- Figure 15. Wear rate as a function of percent polysiloxane rubber, percent TFP in the rubber, and normal load. Indicated bars are 95% confidence limits.
- Figure 16. Main effect of percent rubber on wear rate.
- Figure 17. Main effect of TFP percentage on wear rate.
- Figure 18. Interactive effect of percents rubber and TFP on wear rate; 10N load.
- Figure 19. Interactive effect of percents rubber and TFP on coefficient of friction; 10N load.

LIST OF TABLES

- Table 1. Glass Transition Temperatures of Dimethyl/Methyltrifluoro-propyl Oligomers
- Table 2. Glass Transition Temperatures of Siloxane-Modified Networks
- Table 3. Selected Young's Moduli
- Table 4. Characteristics of Polysiloxane Modifiers, Wear Rates, and Elastic Modulus

Table 1. Glass Transition Temperatures of Dimethyl/Methyltrifluoro-propyl Oligomers

INFLUENCE OF TRIFLUOROPROPYLMETHYL CONTENT ON THE
GLASS TRANSITION TEMPERATURE OF POLYSILOXANES ^(a)

END GROUP	M_n	WT%TFP ^(d)	T _g (°C)
AEP ^(b)	2190	-	- 126
AEP	2330	25	- 116
AEP	2070	50	- 91
AEP	2730	75	- 76
AEP	3130	100	- 58
AEP	1500	100	- 45
PIP ^(c)	1230	100	- 48

(a) DSC, 10°K/min.

(b) Aminoethylpiperazine capped PSX

(c) Piperazine capped epoxy PSX

(d) Weight percent trifluoropropylmethyl SX without end groups

Table 2. Glass Transition Temperatures of Siloxane-Modified Networks

GLASS TRANSITION TEMPERATURES ^(a) OF EPOXY NETWORKS
MODIFIED WITH AMINOETHYLPIPERAZINE CAPPED POLYSILOXANES

\bar{M}_n (g/mole)	2190	2330	2070	2730	3130	1500
<u>Weight%TFP</u> ^(b)	0	25	50	75	100	100
<u>Weight%SX</u>						
0	150	150	150	150	150	150
5	158	157	147	156	150	151
10	153	147	136	156	153	145
15	152	151	150	140	147	140

(a) DSC, 10 K/min.

(b) weight % Trifluoropropyl methyl siloxane without end groups

Table 3. Selected Young's Moduli

TABLE 3. Selected Young's Moduli

<u>SAMPLE</u>	<u>E(10^3 MPa)</u>
CONTROL	1.11 ± 0.17
15-2190-0	0.92 ± 0.09
15-2070-40F	0.95 ± 0.07
15C-3690-10AN	0.88 ± 0.02
15C-3880-17AN	0.86 ± 0.04
15A-2560-10AN	0.68 ± 0.06
15A-1750-18AN	0.77 ± 0.05

Crosshead speed = 1.0 mm/min.

Table 4. Characteristics of Polysiloxane Modifiers, Wear Rates, and Elastic Modulus

TABLE 4. The Characteristics of Polysiloxane Modifiers, Wear Rate, and Elastic Modulus

Sample No.	Characteristics of the Polysiloxane Modifiers			Wear Rate ^(a) 10 ⁻⁹ cm ² /cycle	Elastic Modulus GPa
	Rubber %	Mn	TFP%		
1	0	0	0	6.0	1.11
2	5	2190	0	5.5	1.01
3	10	2100	0	4.5	0.97 ^(b)
4	15	2190	0	0.9	0.92
5	5	2330	20	5.3	1.14
6	10	2330	20	0	0.88
7	15	2330	20	0	0.88
8	10	2540	30	1.8	—
9	10	1500	70	7.1	1.00

^aAverage of wear rates at the normal loads 2,5,10 N.

^bSample for modulus measurement: 10-2190-0

CHEMICAL STRUCTURE OF THE SILOXANE MODIFIERS

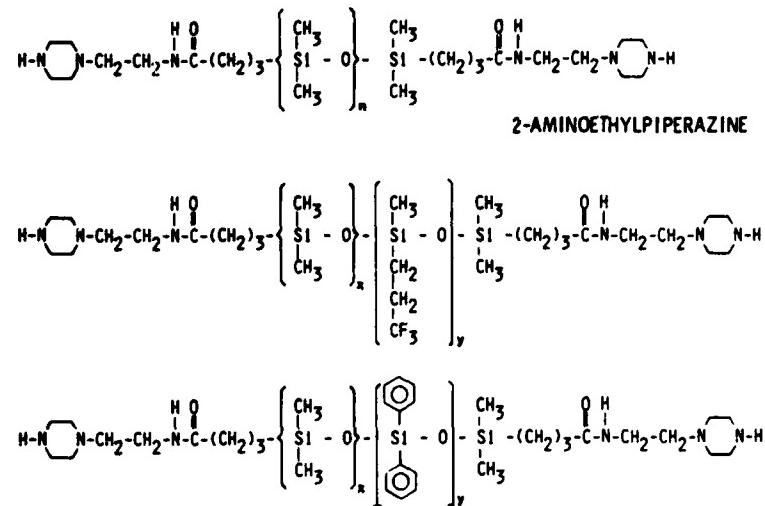


Figure 1. Chemical structures of siloxane oligomers.

NOMENCLATURE

WT. PERCENT -- MOL. WT. OF MODIFIER -- WT. PERCENT
"COMONOMER"

5, 10, 15 1500 - 4000 TFP, DIPHENYL, AN

EXAMPLES

Pure PDMS: 5-2190-0

TFP Siloxane: 10-2070-40F

Diphenyl Siloxane: 5-2250-20D

CTBN: 10C-3880-17AN

ATBN: 15A-2560-10AN

Figure 2. Sample nomenclature for oligomers and modified resins.

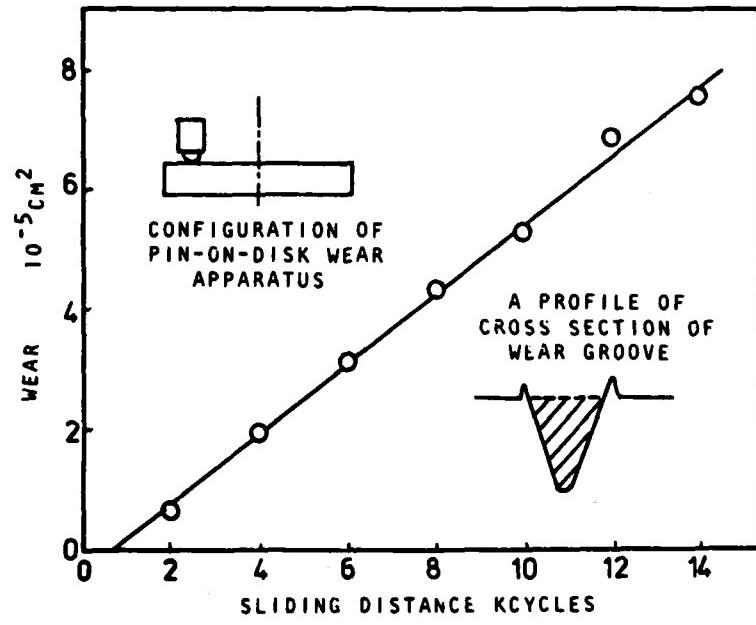


Figure 3. Wear (cross section area) as a function of the number of cycles of disk rotation.

SYNTHESIS OF A SILOXANE MODIFIED EPOXY RESIN

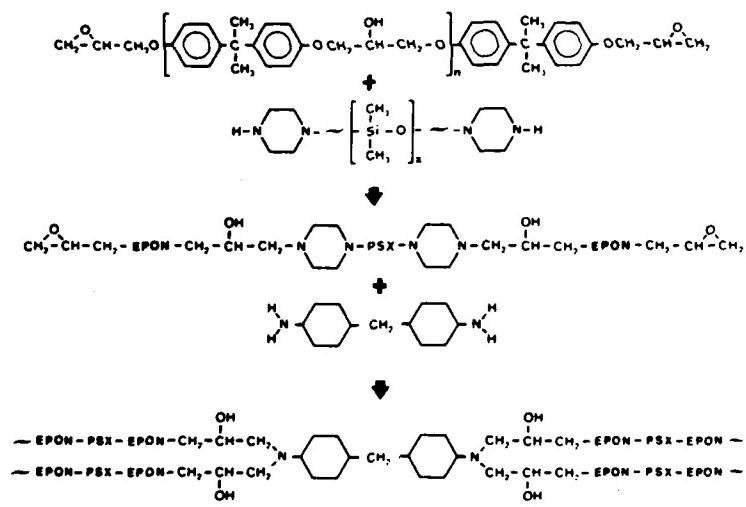


Figure 4. Synthesis of a siloxane-modified epoxy resin.

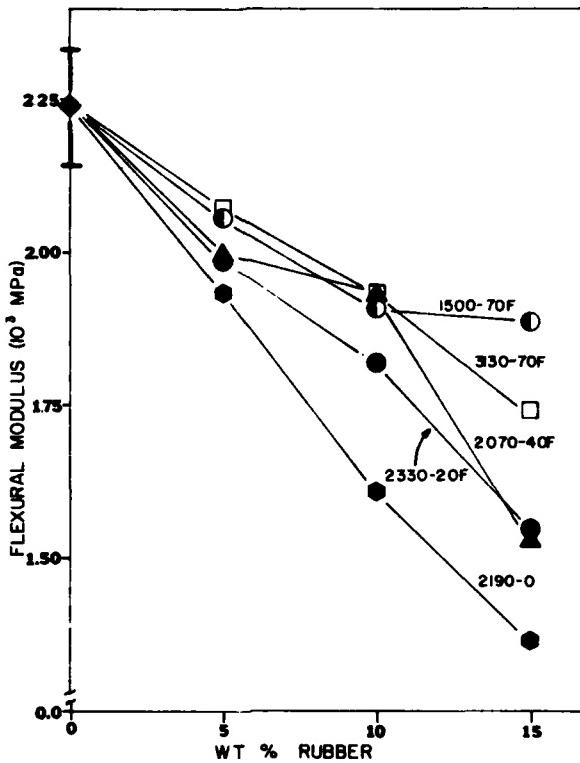


Figure 5. Changes in flexural modulus with rubber content and TFP percentage in rubber. Error bars on data point for control are typical for all data points. Crosshead speed is 1.0 mm/min.

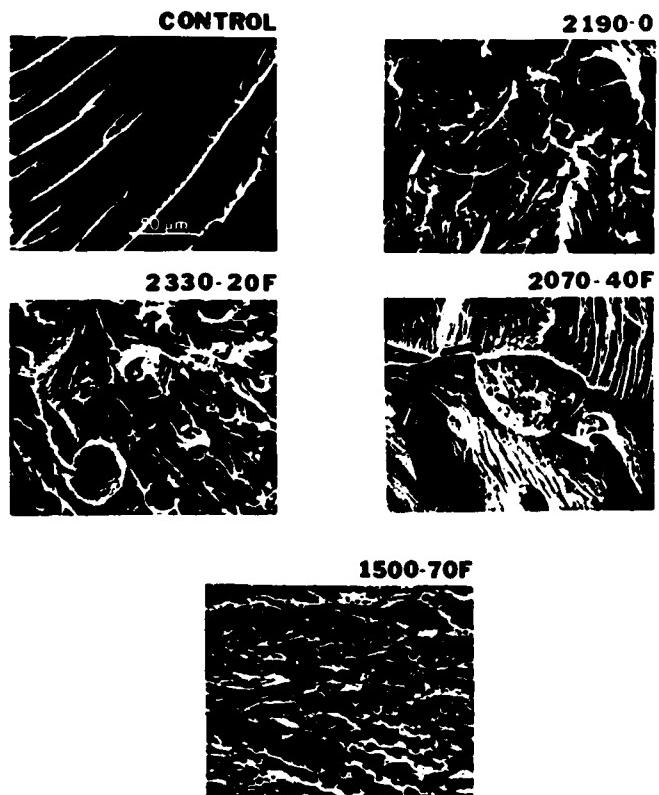
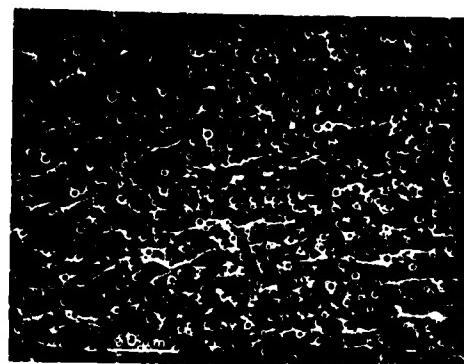
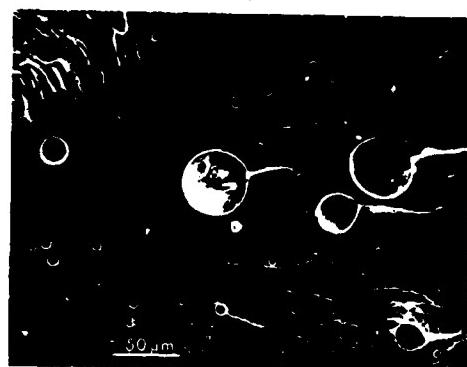


Figure 6. SEM cold snap fracture surfaces for unmodified resin control and four siloxane-modified resins. Original magnification is 300X.



15-1500-70F



15-3130-70F

Figure 7. SEM cold snap fracture surfaces for 15-1500-70F and 15-3130-70F. Original magnification is 300X.

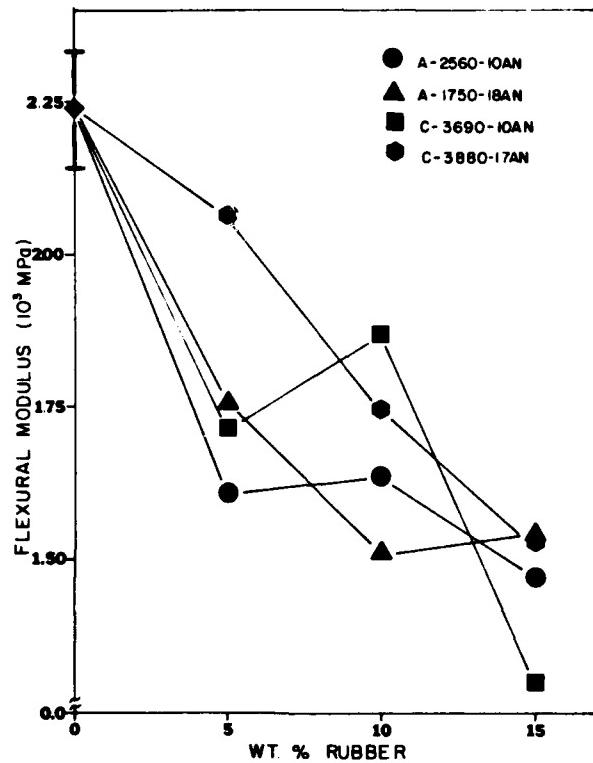


Figure 8. Changes in flexural modulus with rubber content and acrylonitrile (AN) percentage in ATBN and CTBN rubbers. Error bars on data point for control are typical for all data points. Crosshead speed is 1.0 mm/min.

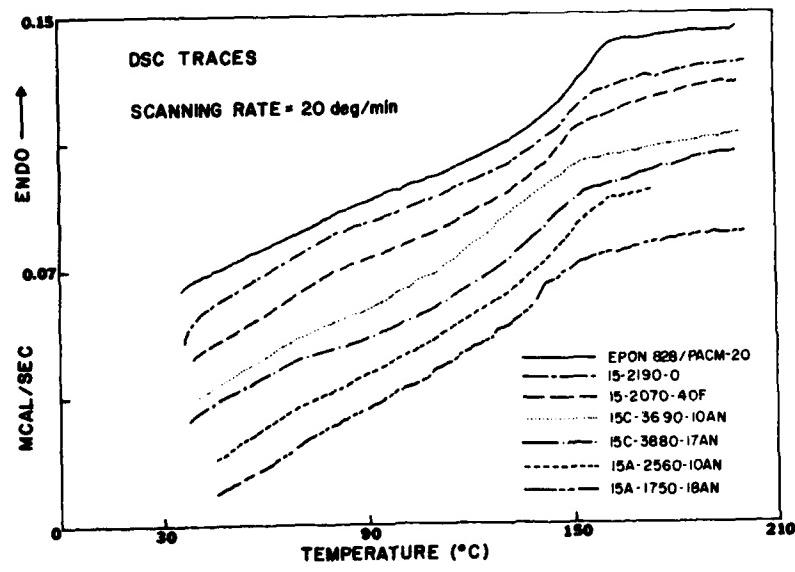


Figure 9. Normalized DSC traces of control and resin modified with 15% of one of six different oligomers. Six of the curves have been shifted vertically.

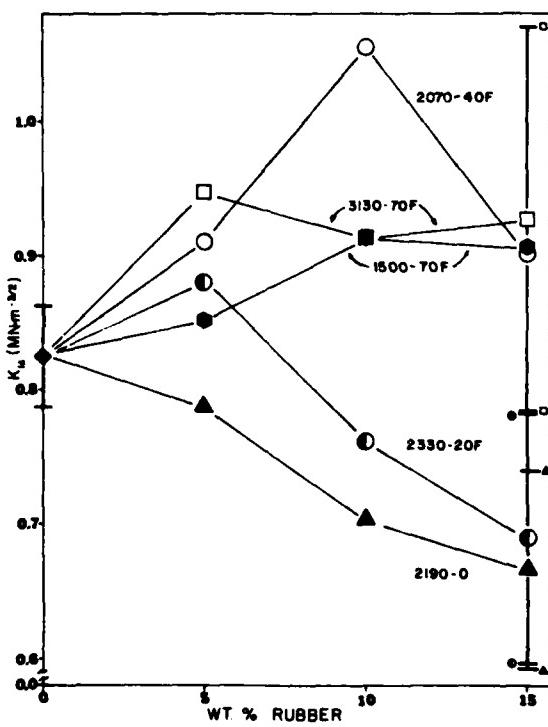


Figure 10. Changes in K_{Ic} with rubber content and TFP percentage in rubber. See text for explanation of error bar usage. Crosshead speed is 0.5 mm/min.

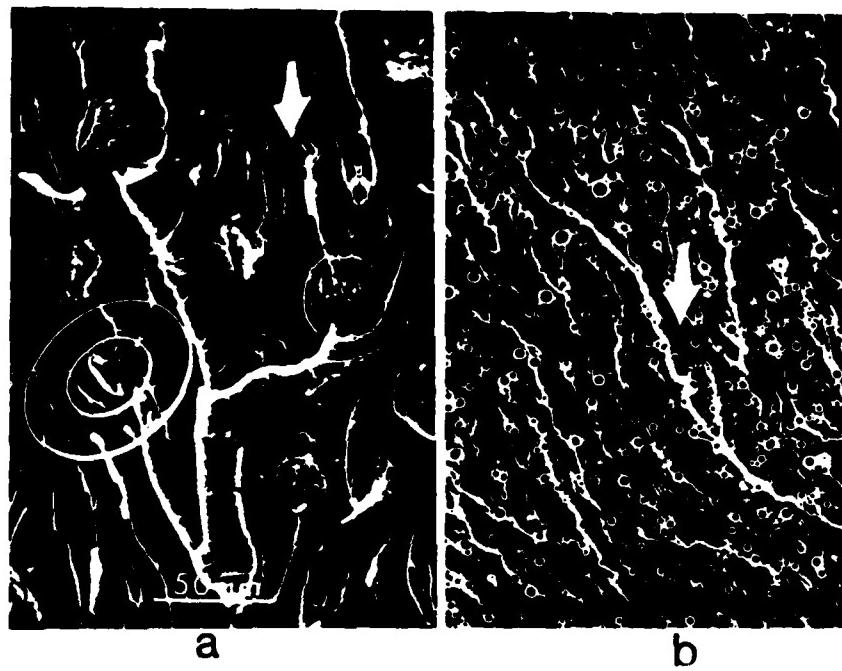


Figure 11. SEM micrographs of pre-crack fronts of fracture toughness specimens: a) 10-2330-20F and b) 15-1500-70F. Ellipses highlight torn rubber domain. Arrows indicate direction of crack propagation. Original magnification is 300X.

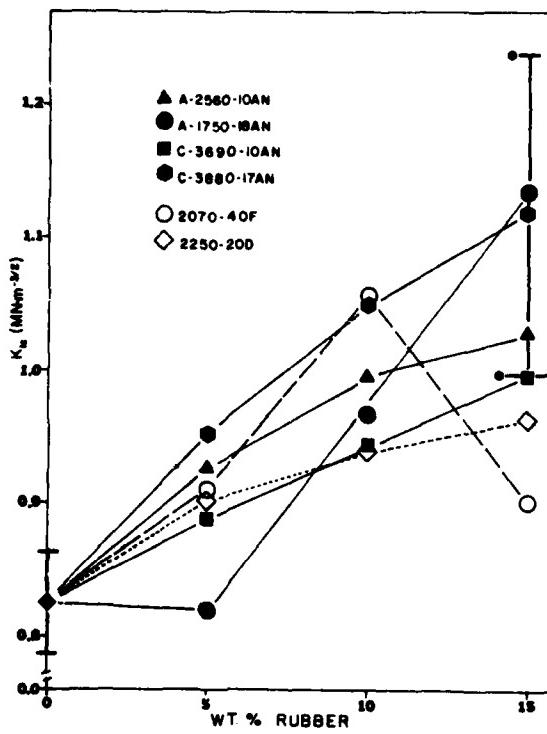


Figure 12. Changes in K_Ic with rubber content for resin modified with ATBN, CTBN, 2070-40F, and 2250-20D. See text for explanation of error bar usage. Crosshead speed is 0.5 mm/min.

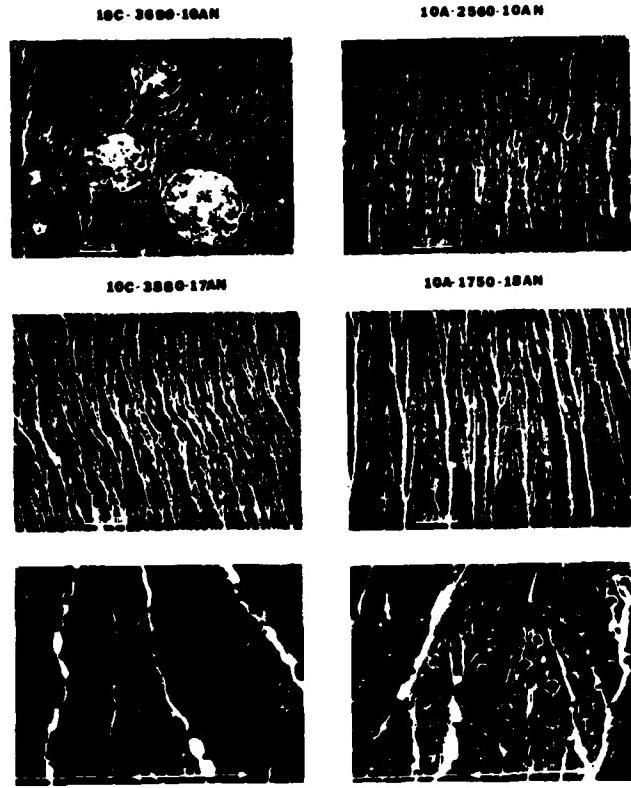


Figure 13. Upper four photomicrographs are low magnification views of K_{Ic} fracture surfaces of resin modified with 10% of each butadiene oligomer. Lower two micrographs magnify the small particles of the two high AN oligomers, elucidating the differences in small particle make-up between the ATBN- and CTBN-modified resins. Original magnifications of upper four are 300X, of lower two, 10,000X.

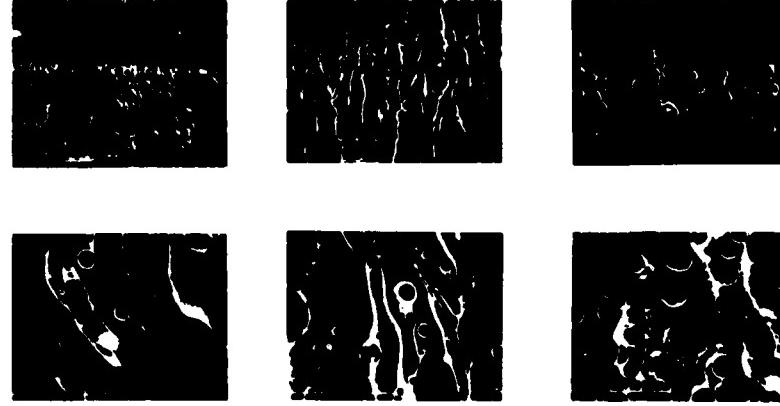


Figure 14. SEM micrographs of pre-crack fronts of resin modified with 2250-20D oligomer. Rubber contents are increasing from 5 to 10 to 15 weight percent moving from left to right.
Original magnification of upper row is 300X, of lower row, 3000X.

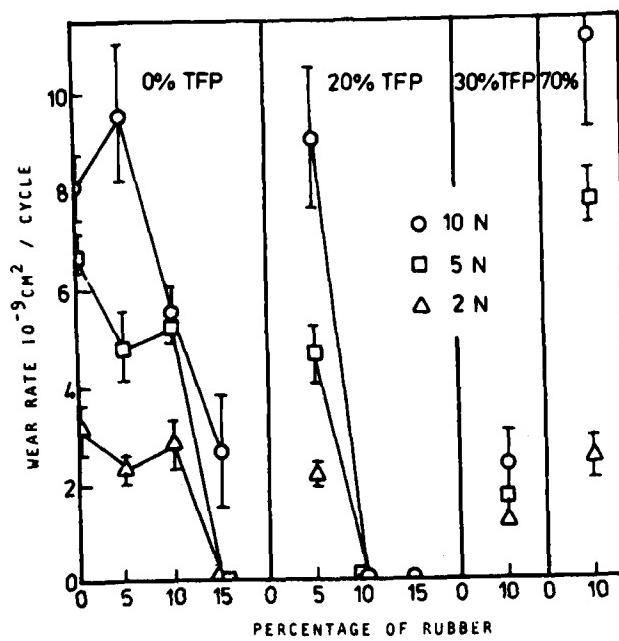


Figure 15. Wear rate as a function of percent polysiloxane rubber, percent TFP in the rubber, and normal load.
Indicated bars are 95% confidence limits.

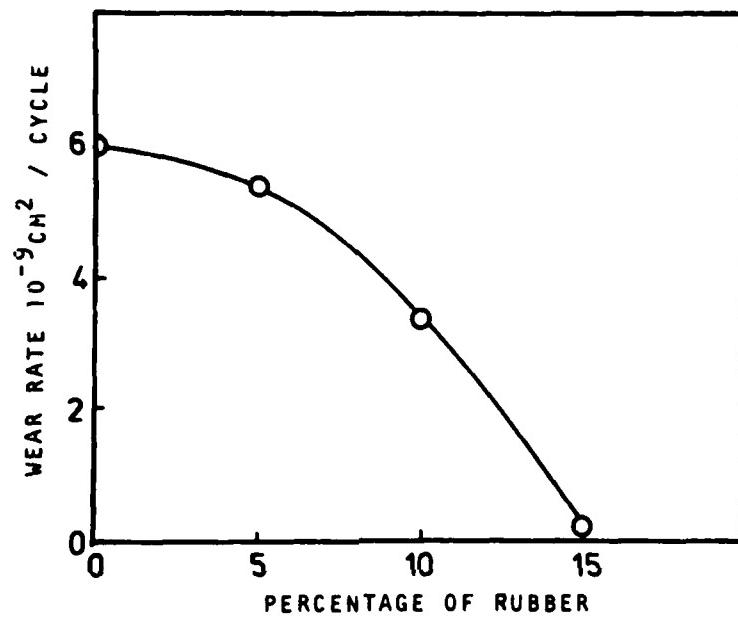


Figure 16. Main effect of percent rubber on wear rate.

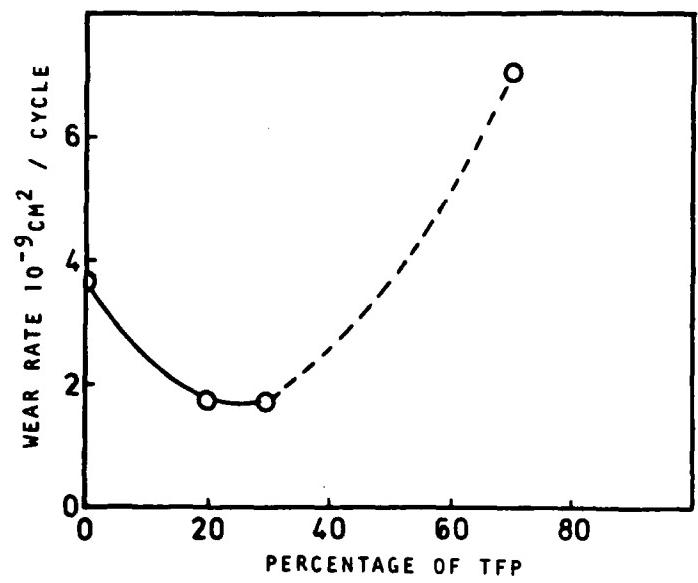


Figure 17. Main effect of TFP percentage on wear rate.

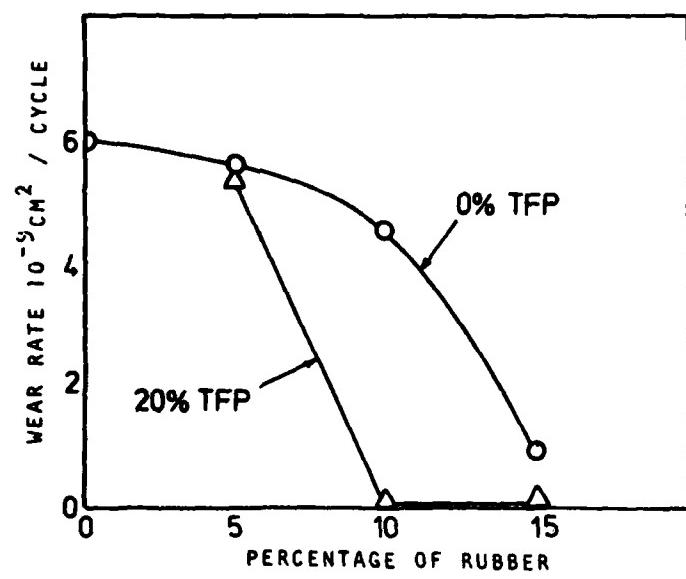


Figure 18. Interactive effect of percents rubber and TFP on wear rate;
10N load.

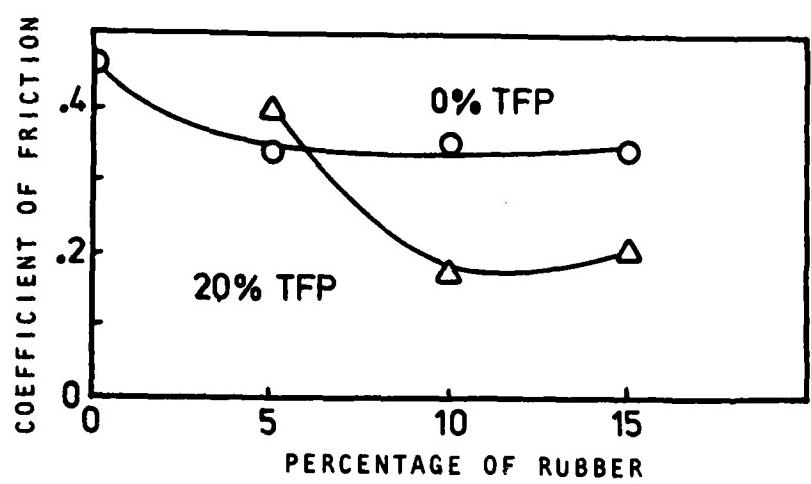


Figure 19. Interactive effect of percents rubber and TFP on coefficient of friction; 10N load.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U. S. Department of Commerce Washington, D.C. 20234	2	Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
Naval Surface Weapons Center Attn: Dr. J. M. Augl, Dr. B. Hartman White Oak Silver Spring, Maryland 20910	1	NASA-Lewis Research Center Attn: Dr. T. T. Serofini, MS-49-1 2100 Brookpark Road Cleveland, Ohio 44135	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1	Dr. Charles H. Sherman Code TD 121 Naval Underwater Systems Center New London, Connecticut 06320	1
Professor Hatsuo Ishida Department of Macromolecular Science Case-Western Reserve University Cleveland, Ohio 44106	1	Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02191	1
Dr. David Soong Department of Chemical Engineering University of California Berkeley, California 94720	1	Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1
Dr. Curtis W. Frank Department of Chemical Engineering Stanford University Stanford, California 94035		Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	
Picatinny Arsenal Attn: A. M. Anzalone, Building 3401 SMUPA-FR-M-D Dover, New Jersey 07801	1	Dr. R. S. Roe Department of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1
Dr. J. K. Gillham Department of Chemistry Princeton University Princeton, New Jersey 08540	1	Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1	Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Dr. Martin Kaufman Code 38506 Naval Weapons Center China Lake, California 93555	1	Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Professor S. Senturia Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor Brian Newman Department of Mechanics and Materials Science Rutgers, The State University Piscataway, New Jersey 08854	1
Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson AFB, Ohio 45433	1	Dr. John Lundberg School of Textile Engineering Georgia Institute of Technology Atlanta, Georgia 30332	1
Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1		
Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	1		
Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	1		
Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	1		
Dr. R. S. Porter Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002	1		
Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	1		

END

FILMED

2 -84

DTIC